

Mapping Heterogeneity in Polymeric Materials Using Atomic Force Microscopy—Phase Imaging and Nanoindentation

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Introduction

Polymer coatings are heterogeneous and often contain degradation-susceptible regions, and corrosion of the metallic substrates has been observed to occur directly underneath these regions (1). The sizes of these regions are believed to range from nanometers to micrometers. Therefore, mapping and identification of heterogeneity in polymer coatings would provide valuable information for understanding the controlled factors and mechanism in the degradation of coatings. Considerable research has been conducted to address this subject. However, little progress has been made due to a lack of suitable analytical techniques.

Atomic force microscopy (AFM) in tapping mode has emerged as a powerful technique to provide direct spatial mapping of surface topography and surface heterogeneity with nanometer resolution (2). Phase contrast in tapping mode AFM often reflects differences in the properties of individual components of heterogeneous materials and is useful for compositional mapping in polymer blends, copolymers and composites. The differences in adhesive or mechanical properties of different components of a heterogeneous sample are expected to influence the energy dissipation at the tip-sample junction, and hence the phase contrast (3). However, attributing phase contrast to specific differences in individual properties of components is difficult. Recently, nanoscale indentation with tapping mode AFM has been explored to provide local mechanical property information in multi-component materials (4). Using phase imaging and nanoindentation in combination allows the heterogeneous regions in polymer materials and systems to be identified.

In this paper, the applications of AFM phase imaging and nanoindentation in unannealed and annealed poly(methylmethacrylate)/polybutadiene blends and a degraded polyester film are presented to demonstrate the utility of these techniques for studies of heterogeneity in polymeric materials. In addition to AFM, other techniques including FTIR, contact angle, DMA and DSC are also used to aid in the interpretation of the AFM results.

Experimental

Materials and Specimen Preparation. Poly(methylmethacrylate) (PMMA) with $M_w = 15,000$ and polybutadiene (PB) with $M_w = 420,000$ were used. PMMA/PB blends were prepared by mixing solutions of a mass fraction of 2% of PMMA and PB in toluene at appropriate ratios. The blends were cast onto pre-cleaned silicon wafers by spin coating at 2000 rpm for 30 s. Samples were analyzed with AFM before and after thermal treatment in an air-vented oven at 80 °C for up to 107 h. Freestanding films of PB, and cast films of PB and PMMA were also prepared so that changes in the PB-rich and PMMA-rich regions of the blends could be compared to the changes in the pure PB and PMMA films. Freestanding PB films and cast PMMA and PB films were annealed at 80 °C in an air-vented oven for different times. At specified time intervals, these samples were removed from the oven for other measurements including contact angle, FTIR, DSC and DMA. Complete experimental details are described elsewhere (5).

Polyester specimens were prepared by mixing isopolyester resin with 2%, by mass, of methyl ethyl ketone peroxide catalyst. Free films of isopolyester were made by molding between two sealed acrylic plates. Poly(ethylene terephthalate) films served as release sheets. Films were allowed to gel at room temperature, followed by a post-cure at 150 °C for 2 h in an air-circulating oven. Polyester specimens were analyzed before and after immersion in an alkaline solution containing 10%, by mass, of NaOH in deionized water at room temperature. The exposed samples were removed from solution at appropriate times, washed with water, and dried with N_2 . Both unexposed and exposed specimens were characterized with AFM.

Atomic Force Microscopy A scanning probe microscope (Dimension 3100, Digital Instruments)[®] was operated in tapping mode under ambient conditions with commercial silicon microcantilever probes. Manufacturer's values for the probe tip radius and probe spring constant are in the ranges of 5

nm to 10 nm and 20 N/m to 100 N/m, respectively. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of $145 \text{ nm} \pm 10 \text{ nm}$. For the majority of investigations discussed in this paper, a set-point ratio (r_{sp}) in the range of 0.70–0.90 was used. For one specific study, however, r_{sp} was varied from 0.18 to 0.84 to study the effect of tapping force level on the phase image contrast. To obtain mechanical response of different domains in the thin films, nanoscale indentation was performed utilizing the same type of silicon cantilever. For this application, force curves were obtained with the tip probing the regions of interest in the blend films. While more in-depth analysis of the force curves can be used to measure relative modulus values, the identity of mechanically different regions can be inferred simply from the slope and shape of the repulsive or contact portion of the force curve (6). This technique was thus used to help identify the PB-rich and PMMA-rich regions in PMMA/PB blends and provide information on the heterogeneity in the degraded polyester films.

Results and Discussion

PMMA/PB System. The dependence of the phase contrast on the tapping force level was investigated for a fixed free oscillation amplitude ($A_0 = 145 \pm 10 \text{ nm}$) using PMMA/PB 20/80 blend. In Figure 1, topographic and phase images of the 20/80 blend are shown for $r_{sp} = 0.84$, $r_{sp} = 0.73$, $r_{sp} = 0.58$, $r_{sp} = 0.51$, $r_{sp} = 0.40$ and $r_{sp} = 0.18$, respectively. As the tapping force level is increased (i.e., r_{sp} is decreased), the contrast changes in both the height images and the phase images in Figure 1. In fact, the contrast in the phase image flips twice, and the topography of the domains relative to the matrix decreases first then increases. Here, the height changes as a function of force level for $0.84 \geq r_{sp} \geq 0.58$ might be an artifact due to coupling between the phase data and the height data, while the height change for $r_{sp} < 0.58$ are possibly caused by deformation of the PB-rich matrix. Flipping of the phase contrast is often observed for light tapping due to the competition between attractive and repulsive tip-sample interaction forces (2,5). Differences in attractive interaction forces due to polarity difference might significantly affect the phase contrast under light tapping conditions. Thus, a change from attractive interaction to repulsive interaction might have caused the flip in phase contrast from $r_{sp} = 0.84$ to $r_{sp} = 0.73$. The second flip in phase contrast from $r_{sp} = 0.51$ to $r_{sp} = 0.40$ could be mainly related to the large deformation of the matrix region (2,5,6).

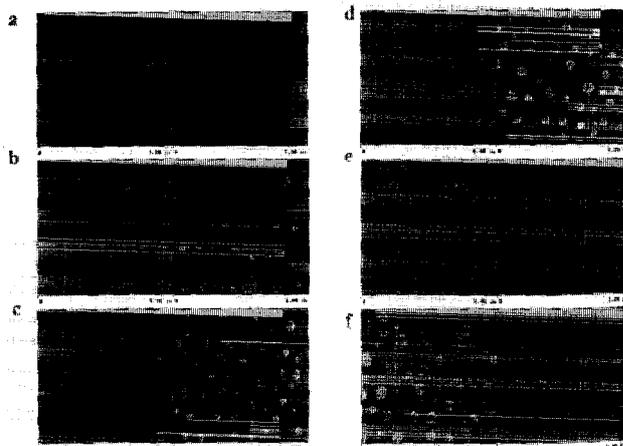


Figure 1. Height images (left) and phase images (right) for PMMA/PB blend sample for various levels of tapping force: (a) $r_{sp} = 0.84$, (b) $r_{sp} = 0.73$, (c) $r_{sp} = 0.58$, (d) $r_{sp} = 0.51$, (e) $r_{sp} = 0.40$, (f) $r_{sp} = 0.18$. Contrast variation 30 nm from white to black for the height images and 90° from white to black for the phase images.

In Figure 2a–2d, topographic (left) and phase (right) images ($r_{sp} = 0.84$) of PMMA/PB 20/80 blend are shown for annealing times of 0 h, 5 h, 20 h, and 107 h, respectively. The morphology of the blend, e.g., spherical PMMA domains in a PB-rich matrix, does not change with annealing. However, phase contrast between the domain and matrix regions decreases with increasing annealing time. In fact, after 107 h of heating (see Figure 2d), phase values of the domains and the matrix are approximately the same.

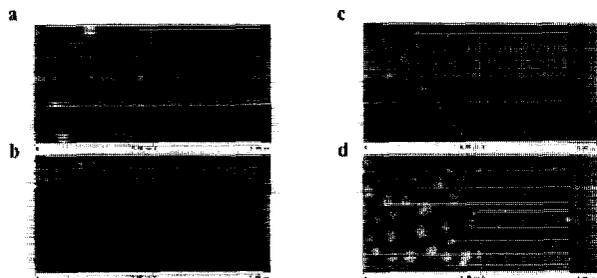


Figure 2. Height images (left) and phase images (right) ($r_{sp} = 0.88$) for a PMMA/PB 20/80 blend sample annealing at 80 °C for (a) 0 h, (b) 5 h, (c) 20 h, and (d) 107 h. Contrast variations are 50 nm from white to black for the height images and 90 ° from white to black for the phase images.

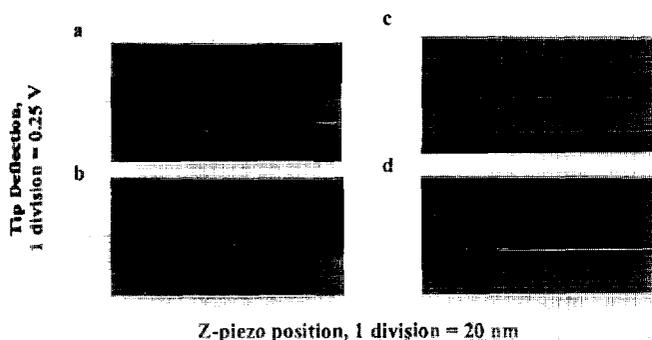


Figure 3. Force curves for the PB-rich matrix of PMMA/PB blend sample annealing at 80 °C for (a) 0 h, (b) 5 h, (c) 20 h, and (d) 107 h.

the heights of the PMMA-rich domains increase with respect to the PB-rich matrix with increasing annealing time.

To study the change in stiffness of the PB-rich matrix of the blends, nanoindentation measurements were performed on the PB-rich and PMMA-rich regions of each PMMA/PB blend sample as a function of annealing time. Force-distance curves for the PB-rich matrix of the 20/80 blend are shown in Figure 3a-3d for 0 h, 5 h, 20 h and 107 h of heating, respectively. The amount of tip penetration into the PB-rich region progressively decreases with increasing annealing time, as noted by the increase in the slope of the repulsive portion of the curve and the decrease in the tip-sample attraction. Furthermore, the force curve of the PB-rich matrix after 107 h of annealing is approaching that of the PMMA-rich domain.

To estimate the changes in chemical and mechanical properties of the PB-rich and PMMA-rich regions during annealing, FTIR, contact angle measurement, DMA and DSC were used to study changes in pure PMMA and PB films. The results show that the extent of oxidation of the PB increases with annealing time up to approximately 100 h, along with the increase in T_g , modulus and polarity of the PB films. On the other hand, no significant changes were observed in PMMA films (5).

Degradation of Polyester. Figures 4a, 4b, and 4c display 3-D topographic images of a polyester film that had been exposed to 10%, by mass, NaOH solution for 0 d, 28 d and 50 d, respectively. Pits of various depths are observed to form on the film surface, and both the depth and

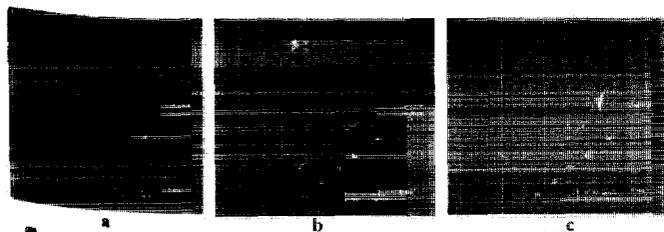


Figure 4. 3-D microstructure of a polyester film exposed to 10%, by mass, NaOH solution for different times: (a) 0 d, (b) 28 d, (c) 50 d. Contrast variations are 400 nm from white to black for the height images.

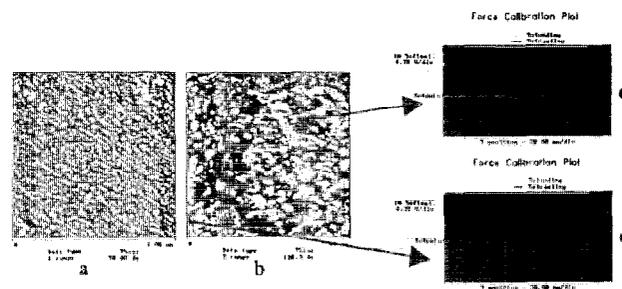


Figure 5. Phase images of a polyester film before (a) and after (b) exposure to 10%, by mass, NaOH solution for 50 days. Figures 5c and 5d are the force curves of the area inside and outside a pit, respectively. Contrast variations are 50 ° for 5a and 120 ° for 5b from white to black in the phase images.

the number of pits increase with exposure time. The microstructure of the pits is quite different, with a higher percentage of the dark areas observed in the phase image compared to that of the unexposed film (see Figure 5a and 5b). Further, force curve results (Figures 5c and 5d) also reveal that the material inside the pit appears to be more compliant than that surrounding the pit. It is noted that the force curves of the film before exposure are similar to those of the area outside the pit, e.g., Figure 5d.

Conclusions

Heterogeneity in polymeric materials was investigated using AFM phase imaging and nanoindentation. The effect of tapping force level on phase image contrast was explored with annealed and unannealed PMMA/PB 20/80 blend samples. Two contrast reversals were observed as the tapping force level was increased. Large decreases in the phase image contrast between the domain and the matrix was observed with increasing annealing time. Also, the stiffness of the PB-rich matrix was found to increase with annealing time using nanoindentation. These phase contrast and stiffness changes corresponded well with changes in the relative chemical and mechanical differences between PMMA and PB, as measured using contact angle, FTIR, DSC and DMA. A combination of phase imaging and nanoindentation was able to show that pits were formed on the polyester surfaces with increased exposure in an alkaline environment and that exposure has resulted in an increase in the heterogeneity in the degraded film.

References

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* Certain commercial instruments are identified in this paper to adequately describe the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments are necessary the best available for the purpose.